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Determination of free carrier lifetimes in semiconductors from the relaxation time of photo-excited infrared absorption

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With 5 figures in the text

ABSTRACT

In semiconductors, an excess concentration of free electrons and holes is generated by light of sufficiently short wavelength. This excess concentration generally decays according to an exponential law governed by the parameter τ, the mean lifetime. The free carriers absorb infrared radiation. Thus the photoelectric effect is accompanied by an increase in the infrared absorption, the relaxation time of which is identical with the carrier lifetime. By periodically interrupting the exciting radiation, it is possible to determine this relaxation time from infrared transmission measurements. It is shown that such a determination may be performed using arbitrarily slow radiation detectors. Application to hole absorption in germanium confirmed the assumption of a definite lifetime. For hole absorption in silicon, it was not possible to decide the constancy of τ, but its order of magnitude was the same as had previously been obtained from photoconductive decay measurements.

Improvements and further applications of the method are suggested.

Introduction

When Q free carriers—electrons or holes—are generated per unit volume and time in a semiconductor, e.g. by photoelectric ionization, then the increase in the carrier density with time can be expressed by the equation

$$\frac{d\Delta n}{dt} = Q - \frac{\Delta n}{\tau}, \tag{1}$$

where t = time and Δn = the excess density of carriers over the equilibrium value n. The parameter τ—the mean lifetime—is in general a function of Δn. It is defined according to equation (1) by the decay rate of the carriers:

$$\frac{1}{\tau} = -\frac{1}{\Delta n}\frac{d\Delta n}{dt}. \tag{2}$$

Numerous investigations [1] have shown that τ is in fact often constant over quite wide ranges of carrier densities and the mean lifetime concept is, therefore, very useful for the description of electrical and optical properties of semiconductors. An interpretation of the nearly constant lifetime in most semiconductors, as well as an explanation of the extreme sensitivity of τ to the purity and structure of the material, has been given by the recombination theory of Shockley and Read and of Hall [2].

In the steady state, equation (1) becomes:

$$\Delta n_s = Q_s \tau, \tag{3}$$

where Q_s is now assumed to mean the number of photoelectrically active photons absorbed per unit time and volume. Thus, the increase in carrier density Δn_s, and hence the increase in the electrical conductivity of the sample, is proportional to Q_s, i.e. to the intensity of illumination, as long as τ is constant. Sublinearity or superlinearity in the photoconductive behavior of a semiconductor sample has the same significance as a lack of constancy of the mean lifetime.

Both electrons and holes in a semiconductor absorb infrared radiation within certain wavelength intervals. (For a review, see [3].) It may therefore be expected that the illumination of a semiconductor crystal by visible or near-infrared radiation should increase the infrared absorption. This effect has indeed been observed both for germanium [4] and for silicon [5]. Thus illumination of a specimen of path length l and absorption coefficient σ per carrier decreases the transparency by a factor

$$T = e^{-\Delta n \sigma l}. \tag{4}$$

From this, it is obvious that the photo-induced absorption will decay with a relaxation time which is identical to the mean lifetime of the absorbing carriers. Such decay measurements would require radiation detectors with time constants less than the lifetimes measured. Now these lifetimes are generally of magnitudes less than a millisecond. In the actual spectral region, beyond a few microns, however, the only applicable detectors are thermocouples, bolometers, pneumatic cells and, in exceptional cases, photoconductive cells which all have response times at least of the same order of magnitude as the carrier lifetimes, and in most cases considerably greater. Yet it is possible, as has already been pointed out in a preliminary note [6], to determine the rise or decay time of the photo-induced absorption from transmission measurements with slow detectors. This paper deals with the theory of such a method and with its application to the determination of mean hole lifetimes in germanium and silicon.

Theory

Suppose that a sample of a semiconductor is exposed to an illumination which is interrupted periodically with a frequency f and with equal lengths for the light and dark half-periods. If there was no relaxation, this would lead to an excess carrier concentration $\Delta n_s = Q_s \tau$ which would be interrupted synchronously with the illumination, c.f. the curve I in Fig. 1. With a finite relaxation time, the variation of Δn with the time is obtained from the solution of equation (1) which is shown by the curve II in Fig. 1. For very long mean lifetimes, or very high frequencies, the curve Δn versus t approximates asymptotically the line III, $\Delta n = \Delta n_s/2$.

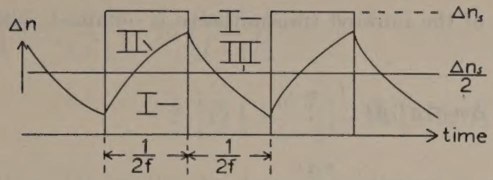

Fig. 1. Density of photo-liberated carriers, Δn, as a function of time for periodically interrupted illumination. Curve I: $f\tau=0$. Curve II: finite $f\tau$. Curve III: $f\tau=\infty$.

The transmittance, T, of the sample for infrared radiation, expressed by equation (4), is time-dependent. A slow detector, e.g. a thermocouple, measures the mean value of T over several periods. Obviously this value becomes for $\tau=0$ or $f=0$:

$$T_0=\tfrac{1}{2}\left(1+e^{-\Delta n_s \sigma l}\right)=\tfrac{1}{2}\left(1+T_s\right), \tag{5}$$

whereas for $\tau\to\infty$ or $f\to\infty$:

$$T_\infty=e^{-\frac{\Delta n_s}{2}\sigma l}=\sqrt{T_s}. \tag{6}$$

We have
$$T_0-T_\infty=\tfrac{1}{2}\left(1-\sqrt{T_s}\right)^2>0.$$

Thus, when the frequency f increases continuously from zero to infinity, the transmittance evidently decreases from T_0 to T_∞.

Solving equation (1) for the dark half-period ($Q=0$) gives:

$$\Delta n_1(t)=Q_s\tau a_1 e^{-t/\tau}. \tag{7}$$

For the illuminated half-period ($Q=Q_s$):

$$\Delta n_2(t)=Q_s\tau\left(1-a_2 e^{-t/\tau}\right). \tag{8}$$

The integration constants a_1 and a_2 depend on the zero point chosen for t. When we put $t=0$ for the beginning of each half-period, then obviously

$$\Delta n_1\left(\frac{1}{2f}\right)=\Delta n_2(0) \quad\text{and}\quad \Delta n_2\left(\frac{1}{2f}\right)=\Delta n_1(0). \tag{9}$$

The conditions (9), inserted into (7) and (8), give:

$$\left.\begin{aligned} Q_s\tau a_1 e^{-1/(2f\tau)}&=Q_s\tau\left(1-a_2\right),\\ Q_s\tau\left(1-a_2 e^{-1/(2f\tau)}\right)&=Q_s\tau a_1.\end{aligned}\right\} \tag{10}$$

With
$$\xi=e^{-1/(2f\tau)} \tag{11}$$

one obtains from (10) $a_1=a_2=1/(1+\xi)$ and thus:

$$\left.\begin{aligned} \Delta n_1(t)&=\frac{Q_s\tau}{1+\xi}e^{-t/\tau},\\ \Delta n_2(t)&=Q_s\tau\left(1-\frac{1}{1+\xi}e^{-t/\tau}\right).\end{aligned}\right| \tag{12}$$

The mean value of the infrared transmittance is obtained, with the aid of (12), from the equation:

$$\begin{aligned} T &= f\int_0^{1/f} \exp\left(-\Delta n(t)\sigma l\right)dt \\ &= f\int_0^{1/(2f)} \exp\left(-\Delta n_1(t)\sigma l\right)dt + f\int_0^{1/(2f)} \exp\left(-\Delta n_2(t)\sigma l\right)dt \\ &= f\int_0^{1/(2f)} \exp\left\{-\frac{Q_s\tau\sigma l}{1+\xi}e^{-t/\tau}\right\}dt + f\int_0^{1/(2f)} \exp\left\{-Q_s\tau\sigma l\left(1-\frac{1}{1+\xi}e^{-t/\tau}\right)\right\}dt. \end{aligned} \tag{13}$$

With the substitution

$$b = \frac{Q_s\tau\sigma l}{1+\xi} = -\frac{\ln T_s}{1+\xi}, \tag{14}$$

the first term in the last member of equation (13) becomes:

$$\begin{aligned} f\tau\int_0^{1/(2f\tau)} \exp\left(-b e^{-x}\right)dx &= -f\tau\int_0^{1/(2f\tau)} \exp\left(-b e^{-x}\right)\frac{de^{-x}}{e^{-x}} \\ &= -f\tau\int_{-b}^{-b\xi} \frac{e^z}{z}dz \\ &= f\tau\left(-\int_{-\infty}^{-b\xi} + \int_{-\infty}^{-b} \frac{e^z}{z}dz\right) \\ &= f\tau\left\{-\mathrm{Ei}\,(-b\xi) + \mathrm{Ei}\,(-b)\right\} \end{aligned} \tag{15}$$

and the last term in (13)

$$\begin{aligned} f\tau e^{-Q_s\tau\sigma l}\int_0^{1/(2f\tau)} \exp\left(b e^{-x}\right)dx &= -f\tau T_s\int_0^{1/(2f\tau)} \exp\left(b e^{-x}\right)\frac{de^{-x}}{e^{-x}} \\ &= -f\tau T_s\int_b^{b\xi} \frac{e^z}{z}dz \\ &= f\tau T_s\left(\int_{-\infty}^{b} - \int_{-\infty}^{b\xi} \frac{e^z}{z}dz\right) \\ &= f\tau T_s\left\{\overline{\mathrm{Ei}}\,(b) - \overline{\mathrm{Ei}}\,(b\xi)\right\}. \end{aligned} \tag{16}$$

Inserting (15) and (16) into (13), and considering (14), gives

$$T = f\tau\left[\left\{-\,\mathrm{Ei}\left(\ln T_s\frac{\xi}{1+\xi}\right) + \mathrm{Ei}\left(\frac{\ln T_s}{1+\xi}\right)\right\} + \right.$$

$$\left. + T_s\left\{\overline{\mathrm{Ei}}\left(-\frac{\ln T_s}{1+\xi}\right) - \overline{\mathrm{Ei}}\left(-\ln T_s\frac{\xi}{1+\xi}\right)\right\}\right]. \qquad (17)$$

Using the equations (11) and (17), the mean transmittance is expressed, by means of the tabulated [7] functions $-\mathrm{Ei}\,(-x)$ and $\overline{\mathrm{Ei}}\,(x)$, as a function of $f\tau$. When the function is normalized by plotting $(T - T_\infty)/(T_0 - T_\infty)$ as a function of $f\tau$, there is practically no difference between the curves for different T_s, provided $T_s > \sim 0.15$. We are, therefore, justified in using the approximation for weak absorption:

$$\frac{T - T_\infty}{T_0 - T_\infty} = 1 - \frac{1-\xi}{1+\xi}\cdot 4f\tau. \qquad (18)$$

Application to hole absorption in germanium and silicon

The valence band in both Ge and Si consists of three sub-bands, two of which coincide for zero crystal momentum [3, 8]. From electron transitions between these sub-bands, infrared absorption bands arise which are considerably more intense than the ordinary intraband absorption. For Ge, these bands are situated in the region 3–16 μ and have been observed both in p-type material and by photo-induction [4]. For Si, the corresponding absorption bands lie at 13–33 μ and have only been observed by photo-excitation [5].

For the determination of the mean lifetime of the carriers causing this absorption, a single crystal of the material of dimensions 5 mm × 10 mm × 15 mm was placed in the infrared beam in front of the entrance slit of a Perkin–Elmer spectrophotometer mod. 13, equipped with NaCl or CsBr optics, according to Fig. 2. The path length was made either 10 or 15 mm. The side surface (10 mm × 15 mm) of the sample was illuminated by a tungsten ribbon lamp or a high-pressure xenon discharge lamp (Osram XBO 1001) using large condenser lenses. By means of a rotating cogwheel, the white light beam could be chopped with frequencies up to 4800 c/sec. The frequency was measured by means of a magnetic pick-up, an audio-frequency generator and an oscilloscope. The lower limit of the available frequency interval was set by the infrared beam chopper, which interrupted the radiation 13 times per second.

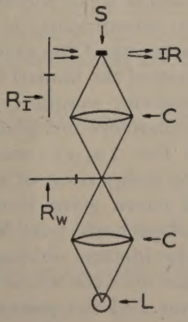

Fig. 2. Arrangement for determining the photo-induced infrared absorption. S, sample; IR, infrared beam; L, white light source; C, condenser lenses; R_I, rotating sector for interrupting the infrared beam (13 c/sec); R_W, cogwheel for interrupting the white light beam (40–4800 c/sec).

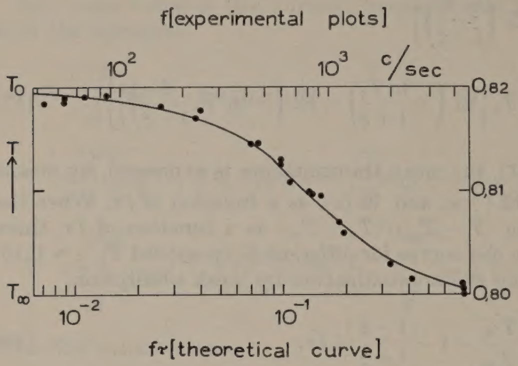

Fig. 3. Mean value of transmittance, T, as a function of $f\tau$ (calculated), and of f, measured at wave-number 900 cm^{-1} for sample of near-intrinsic Ge with resistivity 50 ohm cm. $T_s = 0.64$.

It turned out experimentally that, down to about 40 c/sec, the frequencies of the exciting beam and the infrared beam did not interfere with each other. The infrared chopper was placed in front of the sample so that any scattered white light entering the spectrophotometer was unmodulated and thus gave no signal to the detector.

Results of measurements on single crystals of Ge and Si are shown in Figs. 3, 4 and 5. For the determination of τ, $(T - T_\infty)/(T_0 - T_\infty)$ was plotted against log f. The curve was then shifted horizontally until it fitted the theoretical curve $(T - T_\infty)/(T_0 - T_\infty)$ versus log $f\tau$. The mean lifetime τ could then be immediately obtained by a comparison of the two abscissa scales. For germanium, the photo-induced absorption is strong. Fig. 3 shows the result of measurements at the wave-number 900 cm^{-1}, for a sample of near-intrinsic Ge with a resistivity of 50 ohm cm. It is seen that, within the limits of error, the experimental plots do actually fit the theoretical curve, i.e. there is a constant mean lifetime. This lifetime was found to be $\tau = 165$ μsec with an estimated error of ± 20 μsec. The constancy of τ was checked by measuring T_s as a function of the intensity of the exciting illumination. The relationship between $-\ln T_s = \Delta n_s \sigma l$ and Q_s was found to be strictly linear, indicating according to equation (3) a constant lifetime.

Two p-type silicon samples with resistivities of about 600 and 250 ohm cm were investigated. The mean lifetimes had previously been found from photoelectric decay measurements to be about 70 and 45 μsec respectively. Since the absorption increase, due to illumination, is much smaller for Si than for Ge, the accuracy is less and the scattering of the experimental points greater, as is seen in Figs. 4 and 5. Moreover, because of the limited frequency interval, only part of the curve is obtained for the low-resistivity sample (Fig. 5), and this involves an additional decrease of accuracy. It is therefore not possible to conclude the constancy of the lifetimes for the Si samples. For $\Delta n_s \sigma l$ versus Q_s, however, a straight line was obtained also in these cases. The comparison of the abscissa scales for the experimental points and the theoretical curve gives from Fig. 4, $\tau = 100$ μsec and from Fig. 5, $\tau = 25$ μsec with an error of perhaps ± 20–50 %. The latter value is only of the same order of magnitude as the lifetime obtained photoelectrically. However, it is not very likely that τ is constant over the whole interval of carrier density, or even that the conductivity decay time and the relaxation time of hole absorption are identical.

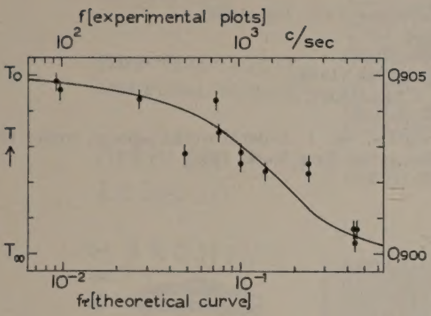

Fig. 4. Mean value of transmittance, T, as a function of $f\tau$ (calculated), and of f, measured at wave-number 300 cm^{-1} for sample of p-type Si with resistivity 600 ohm cm and $\tau = 70$ μsec from photoelectric decay. $T_s = 0.80$.

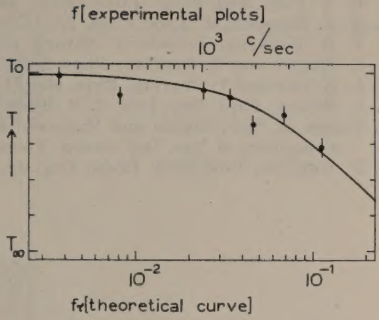

Fig. 5. Mean value of transmittance, T, as a function of $f\tau$ (calculated), and of f, measured at wave-number 700 cm^{-1} for sample of p-type Si with resistivity 250 ohm cm and $\tau = 45$ μsec from photoelectric decay. $T_s = 0.85$.

Improvements and further applications

The effect studied here—the transmittance decrease due to increasing frequency—is of the second order in the absorption coefficient. In fact, for small values of $Q_s \tau \sigma l$, we get

$$T_0 - T_\infty = \tfrac{1}{8} (Q_s \tau \sigma l)^2. \tag{19}$$

As seen from the scattering of the points in Figs. 4 and 5, no high degree of accuracy is obtained for small absorption by the method provisionally applied, which involves a direct measurement of a quantity proportional to T. A better elimination of fluctuations and zero shifts would be obtained by measuring directly $T_0 - T$ or $T - T_\infty$. An apparatus for this purpose is being designed.

The measurements reported here concern the absorption of free holes. It is conceivable that, in some other spectral region, the absorption might emanate from free electrons. Separate determinations of the mean lifetimes τ_n and τ_p for electrons and for holes would then be possible by measurements of the absorption relaxation time in different spectral regions.

Furthermore, the method used in this work should be applicable to the infrared absorption originating from transitions from and to bound electron levels. Determination of the relaxation times for such transitions should help to identify the origins of absorption bands and thus to provide information about recombination mechanisms and energy level diagrams.

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